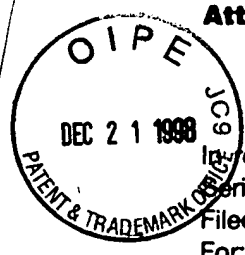


GA 1762

Attorney' Docket N . 50278

PATENT



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Goosey et al. Group No.: 1762
Serial No.: 09 / 172,533
Filed: October 14, 1998 Examiner: Not Yet Assigned
For: ELECTROLESS PLATING PROCESSES

#1 Priority
Paper
2/4/99

Assistant Commissioner for Patents
Washington, D.C. 20231

TRANSMITTAL OF CERTIFIED COPY

Attached please find the certified copy of the foreign application from which priority is claimed for this case:

Country: United Kingdom
Application Number: 9722028.9
Filing Date: October 17, 1997

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SIGNATURE OF ATTORNEY

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NOTE: The claim to priority need be in no special form and may be made by the attorney or agent, if the foreign application is referred to in the oath or declaration, as required by § 1.63.

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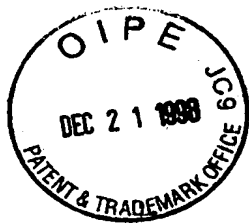
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The Patent Office

The Patent Office
Concept House
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NP9 1RH

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

I also certify that the attached copy of the request for grant of a Patent (Form 1/77) bears an amendment, effected by this office, following a request by the applicant and agreed to by the Comptroller-General.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

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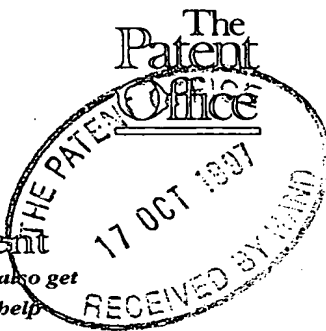
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The Patent Office

Cardiff Road
Newport
Gwent NP9 1RH

1. Your reference

PWC/P20582GB

2. Patent application number

(The Patent Office will fill in this part)

17 OCT 1997

9722028.9

3. Full name, address and postcode of the or of each applicant (underline all surnames)

SHIPLEY COMPANY, L.L.C.,
455 FOREST STREET,
MARLBOROUGH,
MASSACHUSETTS,
U.S.A.

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

73C 586 3001

4. Title of the invention

PLATING OF POLYMERS

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

KILBURN & STRODE
30 JOHN STREET
LONDON
WC1N 2DD

20 2nd Lion Street
LONDON
WC1K 4RJ

Patents ADP number (if you know it)

125001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number
(if you know it)

Date of filing
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
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Description 7

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11. I/We request the grant of a patent on the basis of this application.

Signature  Date 17th October 1997

12. Name and daytime telephone number of person to contact in the United Kingdom

Mr. Paul Chapman
Tel: 0171 242 8291

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PLATING OF POLYMERS

This invention relates to metallization of polymers and more particularly to electroless plating, e.g., copper plating of certain polymers such as ABS (acrylonitrile butadiene styrene) copolymers and other non carbon-fluorine bond polymers.

Conventional methods employed for metallizing polymers (e.g., ABS) utilize aggressive oxidizing agents such as chromic acid as part of the surface treatment prior to conditioning, catalyzation and electroless metal deposition. This results in a lengthy process which often utilizes undesirable chemicals that are both unpleasant to handle and difficult to treat after use. In this invention, a combination of steps is provided which includes a surface treatment providing a substrate morphology which leads after further steps to direct catalyzation of the substrate surface without the need for the traditional subsequent neutralization, conditioning and tin/palladium catalyzation steps. This is a major improvement since it removes several process steps, one of which is the use of chromic acid. The new process is in part based upon the use of electrochemically generated silver²⁺ ions which are able to generate hydroxyl radicals from water. These radicals are very reactive and attack polymer surfaces to give the same type of pitted morphology deemed desirable for subsequent metal adhesion and which is similar to that provided by chromic acid. In this process, following surface texturing the substrate is immersed in a reducing agent pre-dip solution and it can then be plated immediately by immersion in an electroless metal, e.g., copper bath without any further process steps.

The present invention overcomes the above mentioned problems and limitations of the prior art by providing a new and improved method of plating polymers with metal e.g., silver, nickel, gold, cobalt etc. for subsequent use in other applications where molded plastic parts are

used, e.g., in the decorative arts such as in perfume bottle tops and in decorative automobile parts.

The present invention is also useful in the manufacture of printed circuit boards. For example oxidizing agents such as potassium permanganate are used to remove resin smear and to provide a textured polymer surface prior to conditioning, catalyzation and electroless metal deposition. The use of silver $2+$ ions in the production process removes several process steps and reduces chemical consumption.

According to the first aspect of the invention, there is provided a process for metallizing a polymer substrate such as ABS which has been etched by hydroxyl radicals generated from water as a result of the presence of silver $^{2+}$ ions in the water by applying a reducing agent capable of reducing silver ions ($2+$ or $1+$) to the silver metal, e.g., boron hydride or salts thereof such as a sodium borohydride and various boranes such as dimethylaminoborane, sodium dithionite, formaldehyde or a phosphite e.g., sodium hypophosphite, which is preferred, to the polymer substrate and then using electroless plating e.g., using electroless copper to form a metal surface on the polymer substrate. As another aspect of this invention, there is provided a method of plating electroless copper on the polymer substrate e.g., ABS which comprises forming a copper layer on ABS having silver thereon.

As yet a further aspect of this invention there is disclosed the use of electrochemically generated silver $^{2+}$ ions (Ag^{2+} Etch) in a combined surface treatment and metallization process where the silver ions generate hydroxyl radicals capable of texturizing the polymer surface and which can also be reduced to silver metal on the surface so that the silver metal catalyses the subsequent electroless metal to be deposited thereon from a bath thereof, e.g., copper.

In order to achieve good quality metal deposits on polymers such as ABS, their surfaces are normally textured using aggressive solutions that provide a chemically and physically modified surface that is optimized for subsequent conditioning and electroless plating processes. The materials used in the prior art are typically strong oxidizing agents such as the alkali permanganates used with thermosets such as epoxides and chromic acid as used with thermoplastics such as Acrylonitrile Butadiene Styrene (ABS). The aim is to produce a reticulated textured surface that not only is amenable to conditioning with a subsequent surfactant but which also provides good keying and mechanical adhesion of the subsequently deposited electroless copper or other metal. Also, silver²⁺ ions can be generated chemically from solutions of silver⁺ ions by oxidation with strong oxidizing agents such as ozone or by dissolution of silver (II) oxide in acid or by simply dissolving silver (I) fluoride or silver fluorosulphate in acid.

In the case of ABS and chromic acid, the acid preferentially attacks the butadiene groups leaving a surface optimized for subsequent plating. Unfortunately, chromic acid may be a carcinogen and also presents various waste treatment and disposal problems. Accordingly, there is great interest therefore in the development of alternative methods of metallization that do not utilize chromic acid.

Silver ions normally exist in solution as the single charged Ag⁺ ion, as is typically found for example in solutions of silver (I) nitrate, silver (I) tetrafluoroborate, silver (I) perchlorate and silver (I) fluoride. However, although not widely known, under certain conditions silver can be oxidized further to the doubly charged Ag²⁺ ion. This ion is very reactive and can be used to attack virtually all organic materials including polymers. The Ag²⁺ ion in solution is not stable and through a series of reactions converts back to Ag⁺,

typically over a period of a few days. However, the reversion of Ag^{2+} to Ag^+ leads to the generation of hydroxyl radicals and it is this species that is so aggressive towards organic chemical bonds.

Silver $^{2+}$ ions can be generated electrochemically using an undivided or divided cell containing silver (I) nitrate in nitric acid, silver (I) tetrafluoroborate in fluoroboric acid, silver (I) perchlorate in perchloric acid and silver (I) fluoride in hydrofluoric acid or from a mixture of the above mentioned salts and acids. Using an inert electrode such as platinum, platinized titanium, platinum on niobium or tantalum, ruthenium or iridium dioxide on titanium, or carbon (glassy or vitreous) and a current density of 1 mA/sq.cm to 10 A/sq.cm with 500mA/sq.cm being preferred for ABS, the Ag^{2+} ions rapidly form giving a brown solution which readily attacks polymers such as ABS giving a nicely textured surface virtually identical to that produced with chromic acid. Subsequent processing with a reducing agent and electroless metal e.g., copper plating gives electroless copper deposits with adhesion values equal to or better than those from substrates metallized following conventional chromic acid treatment.

It has now been found that if the polymer parts e.g., ABS parts treated with the silver $^{2+}$ process are subsequently immersed in a solution of a phosphite such as sodium hypophosphite or a hydride reducing agent e.g., a borane such as dimethylaminoborane (DMAB) or sodium borohydride, silver remains and the ABS can be immediately plated with electroless metal e.g., copper without any further conditioning or catalyzation steps. The resulting copper deposits have excellent appearance and adhesion. This new process therefore replaces several steps in the conventional chromic acid based process and in particular it removes the need for an expensive tin/palladium catalyst stage. Although without desiring to

be bound to the theory as to what is occurring as a result of using the reducing agent, it is believed that the reducing agent acts to reduce residual silver ions on the polymer substrate to silver metal which is then able to catalyze the electroless copper reaction.

After application of the electroless copper to the polymer substrate, the copper may then be electroplated using conventional technology if desired. It has also been found as another aspect of the invention that applying a solvent swelling system on the substrate prior to etching as taught herein improves the adhesion of the metal to the polymer substrate. For example, solvents such as propylene carbonate, butyrolactone or combinations thereof or methyl ethyl ketone are representative of solvent swelling agents which soften and then swell the polymer surface. A Shipley conditioner product known as PM-920 is useful for this purpose. Also see U.S. Patent No. 5,178,956 regarding conditioners used prior to etching using etchants other than those described herein.

Silver²⁺ (II) was used to treat waste matter (See EP 2 977 738 and U.S. Patent Nos. 4,874,485 and 4,925,643). Also see the paper (3 pages) provided at Science Open Meeting in London, U.K. on May 7, 1997 entitled "New Pretreatments for Polymers", D.M. Brewis, R.H. Dahm and I. Matheson, for the use of silver II and the generation thereof and the one page paper provided at the 1996 Swiss Bonding Meeting entitled, "A New General Method for the Pretreatment of Polymers".

Fig. 1 diagrammatically illustrates the etching of the plastic substrate.

In this figure, there is shown a container 10 which is divided by a cation exchange membrane, e.g., DUPONT NAFION-fluoro polymer cation exchange membrane. At 12, there is shown a platinised-titanium mesh electrode (cathode) coupled to the negative terminal

of a direct current (d.c.) source. An anode 13 of platinised-titanium mesh electrode is connected to the positive terminal +Ve of the d.c. source.

Between the membrane and the anode 13 there is positioned the plastic substrate, e.g., ABS in the shape of a plaque which is to be etched and which is attached to a holder 14A for moving it into and out of the liquid bath 15.

Agitation is provided by a magnetic stirrer (not shown).

The preferred process for metallizing plastics such as ABS include the following steps showing ingredient, amounts, temperature conditions and time.

EXAMPLE 1

PROCESS STEPS	MAKE UP	TEMP/°C	TIME-MINS
1. Apply PM 920 Conditioner (Shipley) to plastic substrate	180 - 250 ml/l	38	1
Rinse (cold water)			2
2. Ag^{2+} Etch	$4\text{M dm}^{-3} \text{HNO}_3 +$ $1\text{ M dm}^{-3} \text{AgNO}_3$ $i=0.5\text{ A/cm}^2$	50	14
Rinse (cold water)			2
3. Apply reducing agent Sodium borohydride	5 g/l	30	1
Rinse (cold water)			2
4. Plate with Cuposit 251 Electroless Copper (Shipley)		46	15
Rinse (cold water)		Room Temperature.	90
5. Electroplate with Electroposit 1200 Copper (Shipley)			90
Rinse (cold water)		Room Temperature	
6. Bake		70	60

EXAMPLE 2

PROCESS STEPS	TEMP/°C	TIME/MINS
1. Apply PM920 Conditioner to plastic substrate	38	1
Rinse	Cold Water Rinse	2
2. Silver Etch ($4 \text{ mol dm}^{-3} \text{ HNO}_3$)	50	14
Rinse	Cold Water Rinse	2
3. Apply 10 g/l Sodium Hypophosphite + 35 ml/l sodium hydroxide $i=0.5 \text{ A/cm}^2$	25	1
Rinse	Cold Water Rinse	2
4. Plate with Cuposit 251 Electroless Copper (Shipley)	46	15
Rinse	Cold Water Rinse	2
5. Apply 10% H_2SO_4 dip	Room Temperature	1
6. Electroplate with Electroposit 1200 Copper (Shipley)	Room Temperature	90
Rinse	Cold Water Rinse	2
7. Bake	70	60

It should be clear that the above process amounts, times, ingredients and etc. may be modified without departing from the invention.

It should also be understood that this process is applicable to polymers other than ABS with exception that the polymers as used herein are not meant to include polymers having carbon-fluorine bonds. Hence the polymers in this application are non-carbon-fluorine bond polymers. Thus the process is useful in the metallization of polyetherimides for use in metallization of molded electrical interconnect devices. The process also has application in the metallization of polymers for electromagnetic energy shielding.

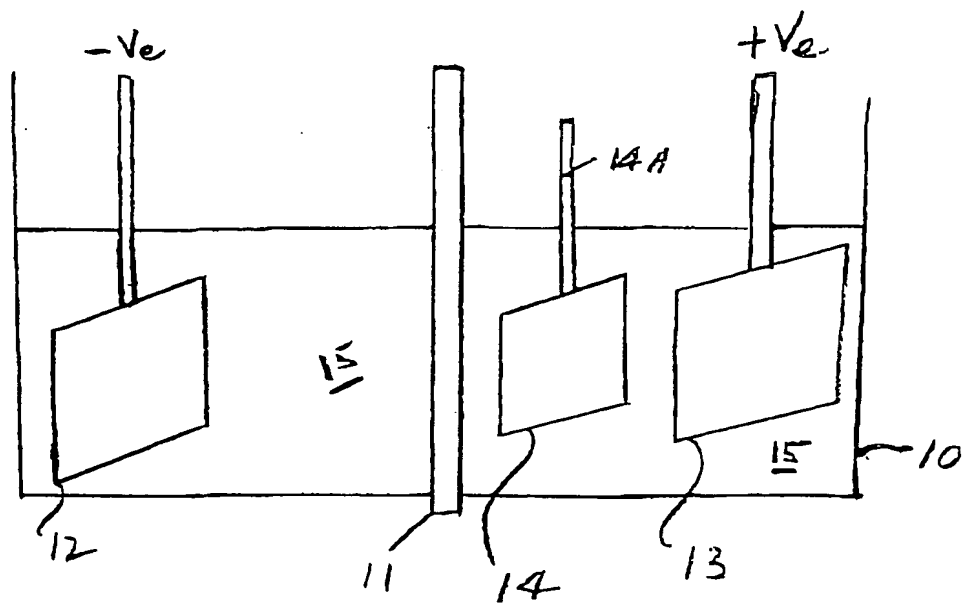


FIG 1

